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A set of $GaAs_{1-x}N_x$ samples with small nitrogen composition ($x<1\%$) were investigated by continuous-wave photoluminescence (PL), pulse-wave excitation PL, and time-resolved PL. In the PL spectra, an extra transition located at the higher-energy side of the commonly reported N-related emissions was observed. By measuring the PL dependence on temperature and excitation power, the PL peak was identified as a transition of alloy band edge-related recombination in GaAsN. The PL dynamics further confirms its intrinsic nature as being associated with the band edge rather than N-related bound states. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1560872]

Heavily nitrogen (N)-doped GaAs, often referred to as a dilute $GaAs_{1-x}N_x$ alloy, has been intensively studied in the past decade. The incorporation of small amounts of N leads to giant band structure changes in the host semiconductor GaAs.[1,2] However, the mechanisms underlying the N-induced band gap reduction remain contentious.[3–5] The results of luminescence and absorption by Makimoto *et al.*[6] suggested that the band gap reduction in dilute $GaAs_{1-x}N_x$ alloy ($x<0.3\%$) starts at a nitrogen-concentration as low as 10^{18} cm^{-3}. Grüning *et al.*[7] investigated the unusual band formation at the Γ point and found that the GaAs-like band edge excitonic state shifts to lower energy with increasing N concentration ($x<0.2\%$) in GaAsN epilayers. When the N concentration was further increased N-cluster states merged into one broadband, which then dominated the photoluminescence (PL) spectra, and the actual PL corresponding to the excitonic band gap gradually became invisible. However, Zhang *et al.* proposed that the impurity band formation from N-induced bound states in GaAs:N played a key role in the band gap reduction,[8] and pointed out that the observed-scaling rule of band gap reduction was supportive of their argument.[9] A recent study of Zhang *et al.* has indicated that the effect of the impurity band formation on the band edge electronic structure critically depends on the band structure of the host material.[10] Very recently, Wang *et al.*[11] explored a PL emission in GaAsN under high magnetic fields and assigned it as an on-set of delocalized states, resulting from the interaction of localized impurity state and the approaching delocalized host state. In theoretical effort, Kent *et al.*[12] explained the evolution of the electronic structure of $GaAs_{1-x}N_x$ from the dilute nitrogen impurity regime to the nascent nitride alloy using empirical pseudopotential method. Up to now, it is unclear as to how and at what composition the GaAsN band edge states remain distinguished from impurity states.

In this work we have investigated a series of heavily doped $GaAs_{1-x}N_x$ samples with small N composition ($x<1\%$) using cw photoluminescence PL, pulse-wave (pw) excitation PL, and time-resolved PL (TRPL). In the PL spectra we have observed an extra transition located on the higher energy side of the previously reported N-related emissions. The relative intensity of this emission is found to increase with increase of either temperature or excitation power. By measuring the PL dependence on temperature and excitation power, we have identified the PL peak as a transition of alloy band edge-related recombination in GaAsN. The PL dynamics further confirms its intrinsic nature, well distinguished from transitions associated with N-related bound states.

The $GaAs_{1-x}N_x$ samples investigated here were grown by gas-source molecular beam epitaxy on semi-insulating (001) GaAs substrates at 420 °C and a growth rate of 0.8 μm/h using a rf nitrogen radical beam source with a mixture of N_2 and Ar in a ratio of 1:9. The epilayer thickness of the samples is nominally 400 nm. Four samples [No. 2658 ($x\sim0.10\%$), No. 2846 ($x\sim0.22\%$), No. 2847 ($x\sim0.36\%$), and No. 2848 ($x\sim0.62\%$)] were used in this study. The detailed growth process has been described elsewhere.[8,10] The N concentration was determined by high-resolution x-ray rocking curve measurements and theoretical dynamical simulations. For cw and pw excitation PL, a Ti sapphire laser, in either cw mode or mode-locked mode, was used as the excitation source. The detection system includes an HR250 single-grating spectrometer and a liquid nitrogen cooled InGaAs photomultiplier tube. The spectral resolution was 0.4 meV. For the time-resolved PL, the Ti:sapphire mode-locked laser was used and the time-correlated signal

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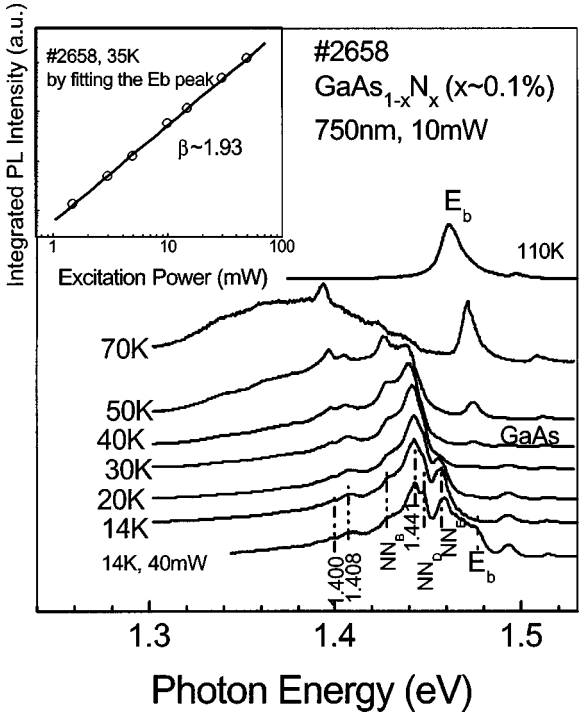

FIG. 1. PL spectra of No. 2658 $GaAs_{1-x}N_x$ sample ($x=0.1\%$) under cw excitation at different temperatures. E_b and a number of N-related bound emissions are denoted in the figure. The inset shows the integrated PL intensity as a function of excitation power.

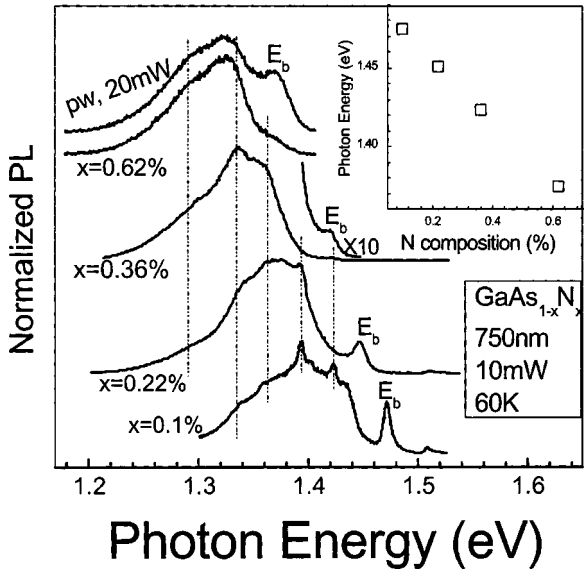

FIG. 2. The PL spectra of all four $GaAs_{1-x}N_x$ ($x=0.1\%-0.62\%$) samples at 60 K and under either cw or pw excitations. At the same time, the exact energy positions of the E_b emissions at 60 K are also shown in the inset.

was analyzed by a two-dimensional synchroscan streak camera with an overall resolution of better than 20 ps.

Figure 1 shows the PL spectra of the No. 2658 $GaAs_{1-x}N_x$ sample ($x=0.1\%$) under cw excitation at different temperatures. It is found that a number of N-related peaks (denoted as NN_E, NN_D, NN_B, 1.441, 1.408, 1.400, and so on) appear in all spectra. These peaks have been previously reported and attributed to different NN_x pairs or N clusters,[6–8,13] although the spectral shape and relative intensity of the peaks may vary in different works. Note that, besides the emissions from the GaAs bulk and C-related shallow impurity, an extra peak, labeled as E_b, was observed at the high-energy side of the earlier-mentioned N-related bound transitions. This peak was observed in all the samples investigated (see Fig. 2). As can be seen from Fig. 1, the intensity of the E_b emission increases with increase of temperature, and it completely dominates the PL spectra at 110 K. Obviously this result is in striking contrast with the temperature behavior of the N-related bound states, which gradually disappear with increasing temperature, due to a thermal activation process, as shown in Fig. 1. In the inset of Fig. 1, we have plotted the integrated PL intensity of the E_b emissions as a function of the excitation power on a double logarithmic scale. The PL intensity is found to increase superlinearly with increase of the excitation power, following a power-law form of $I_{\mathrm{PL}} \propto I_{\mathrm{exc}}^{\beta}$. The measured exponent β is 1.93. All these experimental results suggested that the E_b emission is an intrinsic emission of the GaAsN alloy band edge states. In accordance with this mechanism the observed superlinear increase of the PL intensity of E_b can be attributed to the free carrier population enhancement under higher excitation levels, because the high density of the photogenerated carriers leads to the saturation of the N-related bound states. Similarly, the increase of the relative intensity of the E_b emission with increasing temperature can also be attributed to the enhanced free carrier population. Further evidence for the assignment of the alloy-related emission can be obtained in the TRPL measurement, as discussed later.

Figure 2 displays the PL spectra of all four $GaAs_{1-x}N_x$ ($x=0.1\%-0.62\%$) samples at 60 K and under either cw or pw excitations. As can be seen from the figure, the use of higher temperature and pw excitation in the experiments favors the observation of the E_b emission. In particular, the use of pw excitation can greatly enhance the relative intensity of the E_b emission due to the band-filling effect. For instance, the E_b emissions which are rather weak for samples with $x=0.62\%$ and 0.36% under cw excitation, are now well resolved under pw excitation. With short pulse excitation, the initial position of the electron quasi-Fermi level in the conduction band can be high enough to populate the higher states, resulting in the observation of the high-energy-lying E_b emission. A similar result has been observed in GaAsN/GaAs single quantum well structures[14] and has been attributed to the recombination of delocalized excitons in the quantum wells. Another important feature in the figure is the redshift of the E_b emission energy with increasing N composition. This redshift is in agreement with the theoretical prediction of the GaAsN band-bowing effect.[2,15] At the same time, a number of discrete N-related bound states originating from NN_x pairs or N clusters are also shown in Fig. 2, which are located at energies below the E_b emission. In contrast to the redshift of the E_b emission with increasing N concentration, the energy positions of these bound states appear to be consistent from sample to sample, although the spectral shapes from different samples look quite different and become more broadened with the increase of the N concentration. This consistency is due to the fact that their PL energies are not determined by the N concentration but rather by the distance between N atoms in a pair or cluster. Previous studies have indicated that the spectral shape is very sensitive to the doping level in this range of the doping levels.[6–8] This

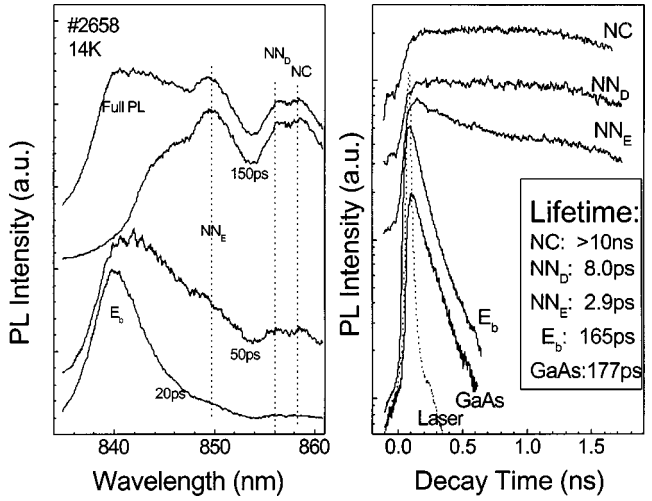

FIG. 3. (a) 14 K time-resolved PL of No. 2658 sample which are detected at 20, 50, and 150 ps, respectively. (b) The decay PL decay curves of No. 2658 sample monitored at GaAs [not shown in Fig. 3(a)], E_b, NN_E, NN_D, and NC.

different evolution of the E_b emission and N-related bound emissions with increasing N composition shows again that the origin of the E_b emission could be completely different from N-related bound states. In the inset of Fig. 2 the peak energy of the E_b emission is plotted as a function of N concentration. E_b has approximately a linear dependence on x with $dE/dx \sim -200$ meV/N% in the N-concentration range of 0.1%–0.62%. Note that E_b follows closely with the excitonic band gap determined by the absorption[10] or photoluminescence excited spectra (PLE),[6,7] but with a small redshift, as in many conventional alloys.

In order to reveal the physical origin of the E_b emission, we have carried out time-resolved PL measurements for the samples. Figure 3(a) shows the low-temperature PL spectra of a GaN_xAs_{1-x} ($x=0.1\%$) sample at different delay times. It can be seen that the E_b emission dominates the PL spectrum immediately after the short pulse excitation (20 ps). With increase of the delay time, a number of N-related emissions appear. At 200 ps the PL spectrum is dominated by N-related emissions, labeled as NC, NN_E, NN_D, etc. PL decay curves monitored at different energies are plotted in Fig. 3(b). One can clearly distinguish two types of carrier dynamics. The decay time of the E_b emission is ~165 ps, comparable to that of the near band gap GaAs emission (170 ps). Whereas the carrier decay times of the nitrogen bound states are much longer: 3 ns for NN_E, 8 ns for NN_D, and more than 10 ns for NC (limited by the instrument). In general, excitons bound in potential minima, will be frozen up in mobility, resulting in a reduction of the spatial coherence, and consequently have a longer lifetime. This happens in the cases of quantum dots and quantum wires where the decrease of the excitonic coherence extension is imposed by the lateral dimensional confinement.[16,17]

In summary we have investigated a set of heavily doped $GaAs_{1-x}N_x$ with small N composition ($x<1\%$) by PL and TRPL. In the PL spectra an extra transition located at the higher energy side of the reported N-related emissions was observed. We have taken advantages of short pulse excitation and PL decay time measurements to clarify the physical origin of the emission. Our experimental results strongly suggest that the PL peak is a band edge transition of the GaNAs alloy rather than a transition from N-related bound states. The GaAsN band edge states remain distinguished from N impurity states at least up to $x=0.62\%$. The importance of this work is to show how the change in the alloy band gap is manifested in its band edge PL in a similar fashion as that in conventional alloys.

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